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(54) Title: BRANCHED CHAIN COMPOUNDS AND THEIR USE (57) Abstract Certain branched chain compounds such as double-tailed alcohol ethoxylates and double-tailed alcohol ether sulfates of specified chemical structures, their synthesis, and their utilities are described.		

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BRANCHED CHAIN COMPOUNDS AND THEIR USETechnical Field

This invention relates to certain branched chain compounds having surfactant properties enabling their use as wetting agents, solubilizing agents, washing agents, dispersing agents, emulsifying agents, and/or scouring agents, and novel intermediates therefor.

Background

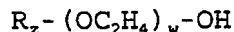
In U.S. Pat. Nos. 3,887,624 and 3,952,068, R. M. Gipson, F. E. Bentley and J. G. Milligan describe vinylidene alcohol compositions having improved properties for surfactant uses as compared to similar prior linear alcohol-based surfactants and prior highly branched alcohol-based surfactants. In addition to primary vinylidene alcohols, these patents disclose ethoxylates of vinylidene alcohols having the formula $R_z''''-(OC_2H_4)_w-OH$ where z is the number of carbon atoms in the alkyl group, R'''' , and w is 7 to 15 and preferably 7 to 12, and represents the average number of oxyethylene groups present in the ethoxylate. Stressed in the patents is the desirability of having the ratio of w to z within the range of 0.685 to 0.755, and also of having z equal to 13 and w in the range of 9 to 10. These two patent disclosures are fully incorporated herein by reference for all purposes.

The Invention

This invention provides as a first embodiment, useful nonionic ethoxylates of certain vinylidene alcohols having less than 7, or an average of less than 7, oxyethylene groups per molecule, and a ratio of the number of ethyleneoxy groups (w) to carbon atoms in the alkyl group (z) of 0.433 or less.

These compounds of the invention have the formula:

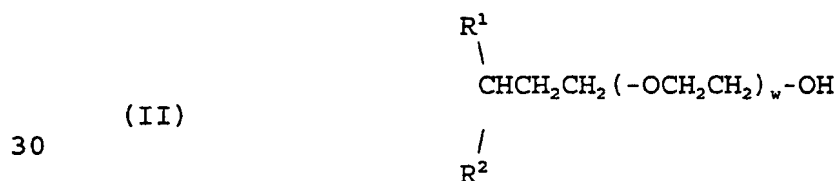
30



(I)

where R is an alkyl group which is bifurcated at the 3-position and each branch has at least 4 carbon atoms (preferably at least 5 carbon atoms, and most preferably at least 6 carbon atoms); z is the number of carbon atoms in R, and is 15 to 33 (preferably 17 to 25); and w is 1 to 6.5 (preferably 2 to 6). It will be seen that the highest ratio of w to z exists when w is 6.5 and z is 15, whereby the ratio w/z is 0.433. Depending on the preparative and if any, recovery and/or purification procedures employed in forming compounds of formula (I), they may be associated with minor amounts (i.e., less than 50 mol%) of other isomers or by-products. As long as the produced, recovered or purified product contains more than 50 mol% of compound(s) of the above formula, it is suitable in the practice of this invention. Preferred products as produced, recovered or purified contain at least 70 mol% of compound(s) of formula (I), and particularly preferred products as produced, recovered or purified contain at least 90 mol% of compound(s) of formula (I). In all cases, however, the requirements remain that w for the product as produced, recovered or purified is 6.5 or less, and that the w/z ratio of such product as produced, recovered or purified does not exceed 0.433.

Formula (II) further illustrates the structure of the major isomer (50 mol% or more) of the compounds of this first embodiment of the invention:



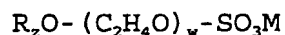
where R¹ and R² are straight chain alkyl groups each having at least 4 carbon atoms (preferably at least 5 carbon atoms, and most preferably at least 6 carbon atoms) and the total number of carbon atoms in R¹ and R² is from 12 to 30 (preferably 14 to 22), and w is as defined above.

A second embodiment this invention provides sulfated

ethoxylates of the above vinylidene alcohols having less than 7, or an average of less than 7, oxyethylene groups per molecule, and a ratio of the number of ethyleneoxy groups (w) to carbon atoms in the alkyl group (z) of 0.433 or less.

5 These compounds may also be referred to as a special type of alcohol ether sulfates.

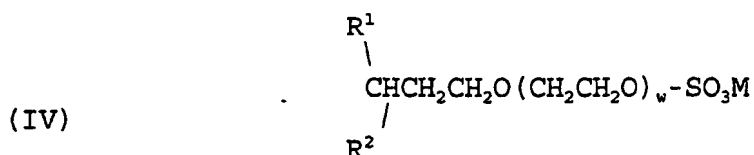
Accordingly, these compounds of the invention have the formula:



10 (III)

where R is an alkyl group which is bifurcated at the 3-position and each branch has at least 4 carbon atoms (preferably at least 5 carbon atoms, and most preferably at least 6 carbon atoms); M is an alkali metal, ammonium, or
15 alkylolammonium (preferably sodium and/or potassium); z is the number of carbon atoms in R, and is 15 to 33 (preferably 17 to 25); and w is 1 to 6.5 (preferably 2 to 6). Depending on the preparative and recovery procedures (and purification procedure, if any) employed in forming compounds of formula
20 (III), they may be associated with minor amounts (i.e., less than 50 mol%) of other isomers or by-products. As long as the produced, recovered or purified product contains more than 50 mol% of compound(s) of the formula (III), it is suitable in the practice of this invention. Preferred products as
25 produced, recovered or purified contain at least 70 mol% of compound(s) of formula (III), and particularly preferred products as produced, recovered or purified contain at least 90 mol% of compound(s) of formula (III). In all cases, however, the requirements remain that w for the product as
30 produced, recovered or purified is 6.5 or less, and that the w/z ratio of such product as produced, recovered or purified does not exceed 0.433.

The following formula (IV) further illustrates the structure of the major isomer (50 mol% or more) of the
35 compounds of this second embodiment of the invention:



5 where R¹ and R² are straight chain alkyl groups each having at least 4 carbon atoms (preferably at least 5 carbon atoms, and most preferably at least 6 carbon atoms) and the total number of carbon atoms in R¹ and R² is from 12 to 30 (preferably 14 to 22), and M and w are as defined above.

10 To prepare the products of this invention, various methods can be used. One preferred method, which starts with an olefin, is:

- 15 a) dimerization of a straight chain 1-alkene using an aluminum alkyl dimerization catalyst to form a vinylidene olefin having one carbon atom less than the desired value for z in formulas (I) and (III) above;
- b) hydroformylation of the vinylidene olefin under typical hydroformylation (oxo) reaction conditions involving
20 reaction with carbon monoxide and hydrogen, and a suitable catalyst (which typically is a complex of cobalt carbonyl or rhodium carbonyl) to produce a branched chain primary alcohol having one additional carbon atom in the 1-position;
- 25 c) ethoxylation of the branched chain primary alcohol with ethylene oxide under typical ethoxylation reaction conditions to form a product of formula (I); and
- d) when forming product of formula (III) above, sulfating the product of formula (I) and neutralizing the sulfated
30 product with the appropriate base.

A route based on use of formaldehyde and hydrogenation in place of the oxo reaction of b) above can be used. As will be seen hereinafter, other methods also can be employed, if desired.

35 Other embodiments and features of this invention appear hereinafter.

The compounds of this invention have a "double tailed"

configuration in a hydrophobic alkyl group, and hydrophilic functionality at the end of the molecule. Hydrophobic and hydrophilic balance is a property of importance for surfactant utilities. Compounds of formula (III) have especially desirable surfactant character due to their amphipathic nature and double tailed configuration. Without desiring to be bound by theoretical considerations, it is believed that by virtue of their of double tailed configuration the water soluble compounds of formula (III) are either incapable or poorly able to form micelles. Instead, these double tailed surfactants tend to distribute as bilayers and afford liquid crystal systems. At a broad range of conditions, these liquid crystal systems are capable of providing very low interfacial tensions which directly results in their desirable performance features.

Methods which can be used to synthesize the compounds of this invention are illustrated by the following examples. A two-step hydroformylation reaction for converting a vinylidene olefin into a primary oxo alcohol is illustrated in Example 1.

Example 1

Synthesis of Intermediate

A 1-liter autoclave is charged with 336 g (1.5 mol) of distilled 2-hexyl-1-decene formed by dimerization of 1-octene using tri-n-octylaluminum catalyst, 10.1 g (0.0295 mol) of $\text{Co}_2(\text{CO})_8$ and 131 g of toluene. The autoclave is sealed, flushed with synthesis gas (H_2/CO), and pressured to 2026 psig at 32°C with synthesis gas and heated to 130°C. Autoclave temperature is maintained at 130°C while synthesis gas pressure is maintained at 3000 psig during repressurization. After 21 hours the autoclave contents are cooled to 32°C, vented and flushed with hydrogen. The autoclave is then pressured with hydrogen to 2370 psig and heated to 190°C. The pressure is then increased to 3142 psig with hydrogen and held under these conditions for 18 hours. The autoclave contents are then cooled to room temperature, vented, flushed with

nitrogen, and discharged. The product mixture is subjected to fractional distillation to recover a fraction boiling in the range of 97-110°C at 0.1-0.4 mm of Hg pressure. In a reaction conducted in accordance with the forgoing procedure a product, shown by nmr to contain 96.3 mol % of primary alcohols, was recovered. The major portion of the product corresponds to 3-hexyl-1-undecanol.

Example 2 illustrates a one-step hydroformylation procedure for producing a primary oxo alcohol for use in preparing a product of this invention.

Example 2

Synthesis of Intermediate

To a 1-liter autoclave are charged 336 g (1.5 mol) of distilled 2-hexyl-1-decene formed by dimerization of 1-octene using tri-n-octylaluminum catalyst, 10.1 g (0.0295 mol) of $\text{Co}_2(\text{CO})_8$, 13.03 g (0.0590 mol) of 9-phenyl-9-phosphabicyclononane, and 146 g of toluene. The autoclave is sealed, flushed with a mixture of hydrogen and carbon monoxide containing approximately 14 wt% hydrogen ($2\text{H}_2/\text{CO}$), pressured to 1097 psig at 22°C, and heated to and held at 200°C. Pressure uptake occurs at about 190°C. When the pressure drops to 1500 psig, the autoclave is repressured to 2000 psig with the same synthesis gas mixture. After 21 hours the autoclave contents are cooled to room temperature, vented and flushed with nitrogen. The autoclave is then pressured with hydrogen to 2370 psig and heated to 190°C. The pressure is then increased to 3142 psig with hydrogen and held under these conditions for 18 hours. The autoclave contents are then cooled to room temperature, vented, flushed with hydrogen, and discharged. The product mixture is stripped of toluene and subjected to fractional distillation to recover a fraction boiling in the range of 120-126°C at 0.15-0.05 mm of Hg pressure. In a reaction conducted in accordance with the forgoing procedure, a product shown by vpc to contain 96.2 area % of primary alcohols was formed. NMR indicated that 75

mol % of the product was 3-hexyl-1-undecanol, along with 22.8 mol % of an isomeric branched chain primary alcohol. The balance (2.2 mol %) was formate ester.

Example 3 illustrates a typical ethoxylation procedure for producing a product of formula (III) of this invention by ethoxylation.

Example 3

Mixed Ethoxylates of 3-Hexyl-1-Undecanol (5:1 Mol Ratio)

To an autoclave are charged 0.5 mol of 3-hexyl-1-undecanol as the 75 mol % product formed as in Example 2, and 0.5 g of potassium hydroxide flakes. While holding the temperature at 140°C, ethylene oxide is slowly charged until 110 g (2.5 mols) of ethylene oxide has been charged. The KOH catalyst is neutralized with oxalic acid, and the product mixture is filtered using filter aid.

Examples 4-11 illustrate the Williamson ether synthesis procedure which can be used.

Example 4

Synthesis of Intermediate

To a 500 mL round bottom flask containing 102.4 (0.4 mol) of $C_{17}H_{35}OH$ (oxo alcohol) formed as in Example 2 and 1.0 g (0.0064 mol) of $C_{10}H_{21}NH_2$ (decylamine) is added 57.1 g (0.48 mol) of $SOCl_2$ (thionyl chloride) at 80°C over a three (3) hour period. Reaction is allowed to continue overnight at 80°C. The reaction mixture is taken up in benzene and washed with water. The organic layer is separated and rotary evaporated at aspirator pressure and 90°C. The organic reaction residue is fractionally distilled to give product boiling at 117-123°C at 0.05 mm Hg pressure. The product is indicated by GC/mass spectral analysis to contain two isomeric forms of $C_{17}H_{35}Cl$. The main isomer is $C_8H_{17}(C_6H_{13})CH-CH_2-CH_2Cl$. The other isomer is $C_7H_{15}CH(CH_2Cl)-CH-C_6H_{13}-CH_3$.

Example 5

Triethoxylate of 3-Hexyl-1-Undecanol

To a reaction flask under a nitrogen atmosphere containing 52.86 g (0.35 mols) of dried $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$ (triethylene glycol) is slowly added pieces of potassium metal (3.42 g, 0.088 mol). After potassium addition is completed, the reaction mass is heated at 100°C for 4 hours. Reaction mass temperature is then increased to 140°C and 20.06 g (0.073 mol) of $\text{C}_{17}\text{H}_{35}\text{Cl}$ from Example 4 is added over 3 hours. Reaction is allowed to continue overnight. GC shows most of the chloride has reacted to give a small amount of C_{17} olefin but mostly the desired $\text{C}_{17}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_3\text{OH}$ where the C_{17} alkyl group of the principal isomer is $\text{C}_8\text{H}_{17}(\text{C}_6\text{H}_{13})\text{CH}-\text{CH}_2-\text{CH}_2-$. The reaction mass is diluted with benzene and washed with water to remove residual triethylene glycol. The benzene solution is rotary evaporated under aspirator pressure and 90°C to remove the benzene. The organic residue is fractionally distilled to give the following a purer product of Formula (III) above, boiling in the range of 187-197°C, mainly $\text{C}_8\text{H}_{17}(\text{C}_6\text{H}_{13})\text{CHCH}_2\text{CH}_2-(\text{OCH}_2\text{CH}_2)_3\text{OH}$.

Example 6

Pentaethoxylate of 3-Hexyl-1-Undecanol

To a 500 mL round bottom flask equipped with stirrer, condenser, thermometer and addition funnel is added 221.56 g (0.93 mol) of pentaethylene glycol $\text{H}(\text{OCH}_2\text{CH}_2)_5\text{OH}$. To this is added 9.36 g (0.24 mol) of potassium metal pieces over 1/2 hour and then the system is heated to 80°C. The reaction mass is stirred at 80°C until the reaction mass is amber and homogeneous. To this reaction mass at 140°C is added over a period of 60 minutes, 54.9 g (0.2 mol) of $\text{C}_{17}\text{H}_{35}\text{Cl}$ (oxo chloride) formed as in Example 4. The reaction temperature is increased to 160°C for 16 hours, then increased to 180°C for 8 hours, and then again increased and held at 200°C for 16 hours. The reaction mass is cooled to room temperature, diluted with benzene and washed with water to remove residual

pentaethylene glycol. The benzene solution is rotary evaporated to remove the benzene, and then is fractionally distilled. The desired product is recovered in the ranges of from 224°C at 0.05 mm to 248°C at 0.2 mm. The product is
5 composed of two isomers, one of which is $C_8H_{17}(C_6H_{13})CHCH_2CH_2-(OCH_2CH_2)_5OH$.

Example 7

Synthesis of Intermediate

To a 3-neck round bottom flask is added 15.3 g (0.32 mol)
10 of $C_{17}H_{35}(OCH_2CH_2)_5OH$ and 0.08 g (0.0005 mol) of $C_{10}H_{21}NH_2$. This is heated to 80°C and 4.59 g (0.0386 mol) of thionyl chloride ($SOCl_2$) is added over 2 hours and allowed to continue at this temperature for 5 hours. The reaction mixture is cooled to room temperature, diluted with pentane and water washed. The
15 pentane solution is dried over anhydrous $MgSO_4$ and rotary evaporated to give over 90% yield of product indicated by GC/mass spectral data to be consistent with $C_{17}H_{35}(OCH_2CH_2)_4-O-CH_2CH_2Cl$.

Example 8

6.4-Ethoxylate of 3-Hexyl-1-Undecanol

To a reaction flask containing dried diethylene glycol, $H(OCH_2CH_2)_2OH$, 13.59 g (0.128 mol) is added 1.25 g (0.032 mol) of potassium metal. The mixture is stirred for 3 hours at ambient temperature and then for 4 hours at 130°C. The
25 temperature is raised to 160°C and 14.74 g (0.0298 mol) of product of Example 7, $C_{17}H_{35}(OCH_2CH_2)_4-O-CH_2CH_2Cl$, is added over 2 hours. The temperature is held at 160°C for 12 hours, at 180°C for 24 hours, at 200°C for 24 hours, and finally at 220°C for 48 hours. The reaction mass is cooled to room
30 temperature, diluted with hexane, washed with water, dried over anhydrous $MgSO_4$, filtered and rotary evaporated at aspirator pressure and 90°C. The organic residue is Kugel-Rohr distilled up to 170°C and 0.4 mm to give a forecut and a pot residue. The pot residue is indicated by GC/mass spectral

analysis to be $C_{17}H_{35}(OCH_2CH_2)_{6.4}OH$, which thus contains the desired isomer $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_{6.4}OH$.

Example 9

Tetraethoxylate of 3-Hexyl-1-Undecanol

5 To a reaction flask containing distilled tetraethylene glycol, $H(OCH_2CH_2)_4OH$, 114 g (0.58 mol) is added 5.75 g (0.147 mol) of potassium metal over a period of 2 hours while maintaining temperature below 65°C. After potassium has reacted, the temperature is raised to 140°C while $C_{17}H_{35}Cl$ (oxo chloride, formed as in Example 4) is added over 2 hours. The temperature is increased to 160°C and kept there for 24 hours. The reaction mass is cooled to room temperature, dissolved in benzene and washed with warm water. The benzene solution is then rotary evaporated and then fractionally distilled to give the desired product: $C_{17}H_{35}(OCH_2CH_2)_4OH$ mainly as two isomers one of which is $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_4OH$.

Example 10

Diethoxylate of 3-Hexyl-1-Undecanol

20 To a round bottom flask is added 42.4 (0.4 mol) of diethylene glycol under a nitrogen atmosphere. To this reaction mass is added 2.3 g (0.1 mole) of sodium over 1 hour. The reaction mass is heated to 130°C whereby all of the sodium has reacted. Then 27.4 g (0.1 mol) of $C_{17}H_{35}Cl$ is added over 1 hour and then kept for 17 hours at these conditions. Reaction temperature is then increased to 140°C and kept for 17 hours at these conditions for 24 hours. The reaction mass upon cooling consists of 2 layers. GC shows the bottom layer to be mostly diethylene glycol. The reaction mass is filtered and the bottom diethylene glycol layer separated. The top organic layer is diluted with diethyl ether, water washed and dried over anhydrous $MgSO_4$. After filtering, the organic layer is fractionally distilled to give a fraction at from 200-220°C and 2.25-2.5 mm containing the desired product, $C_{17}H_{35}O(CH_2CH_2O)_2OH$, in two isomeric forms, one of which is the

desired isomer of this invention, namely $C_8H_{17}(C_6H_{13})CHCH_2CH_2-(OCH_2CH_2)_2OH$.

Example 11 sets forth a general procedure suitable for use in converting the ethoxylates of this invention into the sulfated double tailed alcohol ethoxylates (alcohol ether sulfates) of this invention.

Example 11

Sulfated Ethoxylates of 3-Alkyl-1-Alkanols

To a 3-neck round bottom flask equipped with nitrogen jacketed addition funnel, mechanical stirrer, thermometer and gas exit tube is added the 3-alkyl-1-alkanol compound(s) of this invention to be sulfated. An equivalent amount up to 4% excess of chlorosulfonic acid is added over a period of 30 to 60 minutes, while maintaining the temperature below 30°C if the system is homogeneous, or at 40 to 55°C if a solid phase exists. The reaction mixture is then stirred for an additional 30 minutes or until HCl evolution ceases or at least has slowed down substantially. At this point an equivalent of the selected base, such as sodium hydroxide, potassium hydroxide, or ammonium hydroxide, is added together with sufficient water to form a 10% to 30% solution.

Another useful method of making the double-tailed alcohol ether sulfates of this invention is to react the compounds of formula (I) above with sulfur trioxide in a falling-film reactor, followed by neutralization with a suitable base. For example use of aqueous sodium hydroxide enables the formation of thick slurries, paste, or fluid emulsions of the alcohol ether sulfates, depending upon the amount of water present.

The excellent effectiveness of the compounds of this invention is illustrated by the comparative experiments described in Example 12, wherein the surfactant of this invention is a double-tailed alcohol ether sulfate $(C_8H_{17}-C_6H_{13})CHCH_2CH_2O(CH_2CH_2O)_3SO_3Na$.

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Example 12

Sulfated triethoxylate of 3-hexyl-1-undecanol was compared against the leading commercial pre-wash spray-on product for effectiveness as a pre-soak brightener for laundry use with hard water. The pre-soak formulation used for the sulfated ethoxylate of this invention was composed by weight of 6.4% of the sulfated triethoxylate of 3-hexyl-1-undecanol, 4.1% of 1-butanol co-surfactant, 4.4% of sodium chloride, 6.2% of mineral oil, and 78.9% of water. The commercial product is understood to contain a total of about 18.5% of four active surface active agents with the balance being water. Standard soiled-swatches of cotton cloth were dipped in one or the other of the respective formulations for 5 seconds, a period sufficient for achieving saturation. The treated swatches were then allowed to stand for specified time periods before being washed in a washing machine in the presence of a measured quantity of a commercial laundry detergent product. Water of 50 ppm. (wt/wt) hardness (a 3:2 ratio of $\text{Ca}^{++}/\text{Mg}^{++}$) was used for the wash. Non-treated soiled swatches were also included in the wash as a control. After washing, the swatches were dried in a tumble dryer. The reflectance of the respective swatches was then measured using a Hunterlab Tristimulus Colorimeter, model D25M-9. The results of these tests are summarized in the table in which the values for the untreated cloth is the averaged measurements on 6 untreated cloths.

Table

Surfactant(s)	Time Treated, minutes	<u>L</u>	<u>a</u>	<u>b</u>
Invention	10	76.07	0.92	5.06
Invention	5	75.84	0.97	4.98
Invention	1	75.50	0.88	5.35
Average:		75.80		
Commercial	10	74.46	0.93	5.44
Commercial	5	74.34	0.96	5.16
Commercial	1	73.03	0.89	5.71
Average:		73.94		
None	Untreated	69.71	0.96	6.16

10 Experience has shown that a difference of 1.0 unit in the Hunter "L" value is statistically significant. The results thus indicate that the surfactant of the invention was more effective than the commercial combination which contains a substantially larger amount of surfactants.

15 The usefulness of the double-tailed ethoxylates of this invention as intermediates to useful detergent or surfactant products having enhanced oil-solubility is illustrated by their utility in forming such compounds as double-tailed alcohol ether sulfonates and double-tailed alcohol ether phosphates. The double-tailed alcohol ether sulfonates of this invention are useful as lubricant additives whereas the double-tailed alcohol ether phosphates are useful in the formulation and application of detergents for commercial cleaning, hard-surface cleaners, liquid metal cleaning formulations, and similar products. Example 13 illustrates the production of double-tailed ether sulfonates pursuant to this invention.

Example 13

Tosylate of Tetraethoxylate of 3-Hexyl-1-Undecanol

30 To a round bottom flask are added 20 g (0.046 mol) of tetraethoxylate of 3-hexyl-1-undecanol (Example 9) and 14.54

g (0.164 mol) of pyridine. At an initial temperature of 40°C, 9.72 g (0.051 mol) of p-toluenesulfonyl chloride is slowly added over a one-hour period as the reaction is exothermic. The mixture is then stirred at 50°C for 16 hours. The reaction mixture is diluted with diethyl ether and the solids are filtered off. The ethereal solution is washed with water and if an emulsion results, it is broken by addition of toluene followed by ethanol. The aqueous and organic phases are separated and the organic phase is dried over anhydrous MgSO₄. The dried organic phase is filtered and rotary evaporated at 28 inches of Hg pressure and 90°C. The residual dark liquid is the desired tosylate.

To prepare the double-tailed alcohol ether phosphates of this invention, the compounds of formula (I) above are reacted with a suitable phosphating agent such as phosphorus pentoxide or phosphorus oxytrichloride followed by a neutralization step with a base such as a metal hydroxide (e.g., NaOH, or KOH), ammonium hydroxide, or like basic materials.

The compounds of this invention can be used in combination with other detergents, such as the detergents set forth in the listing of classes and species of detergents in U.S. Pat. No. 3,852,211 to Ohren issued December 3, 1974, the full disclosure of which patent is incorporated herein by reference for all purposes. Thus, merely for the purposes of illustration and not limitation, the compounds of this invention can be used with such detergent types and components as are described in Columns 7-10 of U.S. Pat. No. 4,019,998 issued April 26, 1977 to Benson et al, the full disclosure of which patent is incorporated herein by reference for all purposes. The compounds of this invention can also be used in combination, with or without other detergents, with ion exchange materials and builders such as aluminosilicates, zeolites, sodium tripolyphosphate, sodium pyrophosphate, and other builders such as are referred to as "auxiliary builders" in columns 13 and 14 of Krummel et al. U.S. Pat. No. 3,985,669 issued October 12, 1976, the total disclosure of which patent

is incorporated herein by reference for all purposes. Such "auxiliary builders" can be used in combination with aluminosilicate builders, or they can be used without use of an aluminosilicate. The compounds of this invention can be used in producing spray-dried granular detergent compositions, for example in accordance with the teachings of Ohren et al. U.S. Pat. No. 4,019,999 issued April 26, 1977, the entire disclosure of which patent is incorporated herein by reference for all purposes. Additional components which can be used in formulations containing one or more compounds of this invention include those referred to in any of the foregoing patents to Ohren, to Benson et al., to Krummel et al., and to Ohren et al, or in any reference cited in any one or more of these patents. As illustrated in Example 12 above, the double-tailed alcohol ether sulfates of this invention are particularly effective when used in pre-soak formulations in combination with a co-surfactant such as an alcohol or a glycol ether. Besides the exceptional effectiveness of such compositions, an additional advantage of the double-tailed alcohol ether sulfates of this invention is that microemulsions can be formed using less of such co-surfactants that required in prior formulations for pre-soak usage.

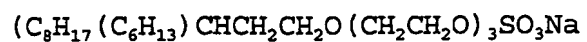
Claims

1. A compound of the formula $R_z-(OC_2H_4)_w-OH$ where R is an alkyl group which is bifurcated at the 3-position and each branch has at least 4 carbon atoms; z is the number of carbon atoms in R, and is 15 to 33; and w is 1 to 6.5.
2. A compound of Claim 1 wherein each said branch has at least 5 carbon atoms.
3. A compound of Claim 1 wherein each said branch has at least 6 carbon atoms.
4. A compound of Claim 1 wherein z is 17 to 25.
5. A compound of Claim 1 wherein w is 2 to 6.
6. A compound of Claim 1 wherein each said branch has at least 6 carbon atoms, wherein z is 17 to 25, and wherein w is 2 to 6.
7. A compound of Claim 1 having the formula $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_2OH$.
8. A compound of Claim 1 having the formula $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_3OH$.
9. A compound of Claim 1 having the formula $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_4OH$.
10. A compound of Claim 1 having the formula $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_5OH$.
11. A compound of Claim 1 having the formula $C_8H_{17}(C_6H_{13})CHCH_2CH_2(OCH_2CH_2)_{6.4}OH$.
12. A compound of the formula $R_zO-(C_2H_4O)_w-SO_3M$ where R is an alkyl group which is bifurcated at the 3-position and each branch has at least 4 carbon atoms; M is an alkali metal, ammonium, or alkylammonium; z is the number of carbon atoms in R, and is 15 to 33; and w is 1 to 6.5.
13. A compound of Claim 12 wherein each said branch has at least 5 carbon atoms.
14. A compound of Claim 12 wherein each said branch has at least 6 carbon atoms.
15. A compound of Claim 12 wherein z is 17 to 25.
16. A compound of Claim 12 wherein w is 2 to 6.

17. A compound of Claim 12 wherein each said branch has at least 6 carbon atoms, wherein z is 17 to 25, and wherein w is 2 to 6.

18. A compound of Claim 12 wherein M is sodium or potassium.

19. A compound of Claim 12 having the formula



INTERNATIONAL SEARCH REPORT

Inter: al Application No
PCT/US 96/10634

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C43/11 C07C305/06 //C11D1/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 20773 (ETHYL CORPORATION) 26 November 1992 see page 3, line 20 - page 4, line 1; examples I,II	12-19
X	US,A,3 887 624 (R. M. GIPSON) 3 June 1975 cited in the application see column 3, line 35 - column 7, line 68; claims; examples IX,XIV,XX	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

18 September 1996

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INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/US 96/10634

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>JOURNAL OF COLLOID AND INTERFACE SCIENCE, vol. 147, no. 2, December 1991, pages 403-406, XP000602370 R. VARADARAJ ET AL: "Relationships between dynamic contact angle and dynamic surface tension properties for linear and branched ethoxylate, ethoxysulfate, and sulfate surfactants" see figure 1; table 1 -----</p>	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/10634

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9220773	26-11-92	NONE	
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		BE-A- 800582	07-12-73
		CA-A- 1049046	20-02-79
		DE-A- 2329518	20-12-73
		FR-A- 2189356	25-01-74
		GB-A- 1438011	03-06-76
		GB-A- 1438012	03-06-76
		NL-A- 7307917	11-12-73